Journal of Magnetism and Magnetic Materials 0 (2008) 1–0

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A critical discussion of calculated modulated structures, Fermi surface nesting and phonon softening in magnetic shape memory alloys $Ni_2Mn(Ga, Ge, Al)$ and $Co_2Mn(Ga, Ge)$

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Abstract

A series of first principles calculations have been carried out in order to discuss electronic structure, phonon dynamics, structural instabilities and the nature of martensitic transformations of the Heusler alloys $Ni_2Mn(Ga, Ge, Al)$ and $Co_2Mn(Ga, Ge)$. The calculations show that besides electronic pecularities like Fermi–surface nesting, hybridizing optical and acoustic phonon modes are important for the stabilization of the modulated martensitic structures.

PACS: 61.66.Dk; 63.20.Dj; 64.70.Rh

Keywords: Heusler alloys; Phonon instabilities; Incommensurate phase

1. Introduction

In this paper, we discuss microscopic details of the structural instabilities observed in ferromagnetic Heusler alloys like the magnetic shape-memory (MSM) system Ni-Mn-Ga [1]. These alloys are of technological importance being used for mechanical applications based on specific elastic properties of the martensites. Due to ferromagnetic order magnetic fields allow to control the crystal structure. Ni_2MnGa has now become a reference system for all investigations related to the MSM technology. It has been shown that in moderate fields of the order of 1 T, the structural deformations in Ni_2MnGa can reach ∼10% [2]. This makes the MSM technology important for new kinds of micro-mechanical sensors and actuators [3]. Serious attemps are undertaken to search for new systems which would show even better MSM performance [4].

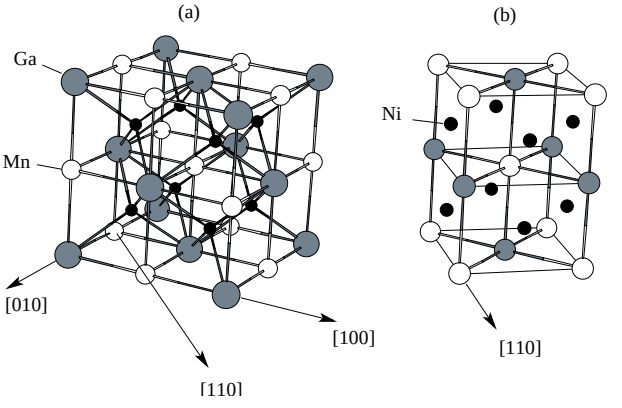

Fig. 1. (a) The cubic $L2_1$ structure of the Heusler alloy Ni_2MnGa. The tetrahedrally coordinated structure of Ga around Ni is clearly visible. Mn also forms a tetrahedral coordination, but in case of Ga the *p*-electrons are able to couple covalently to the Ni atoms. (b) Reduced tetragonal structure used in the calculations.

The MSM effect is a completely material dependent property related to the different kinds of martensite formed at corresponding working conditions. A

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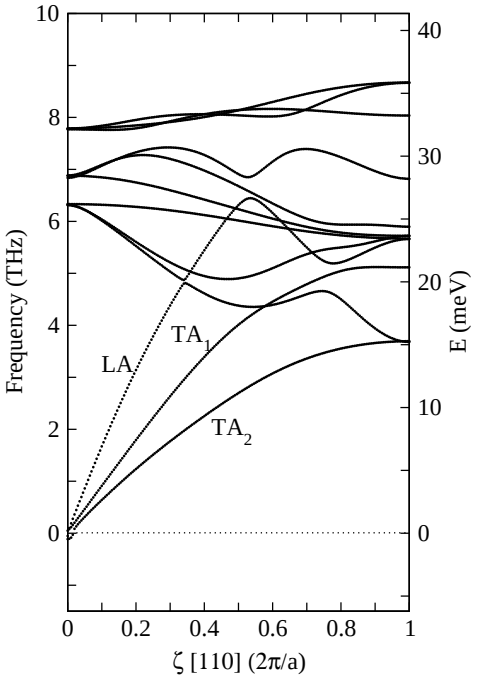

Fig. 2. Calculated phonon dispersions for the cubic $L2_1$ structure of Co_2MnGe.

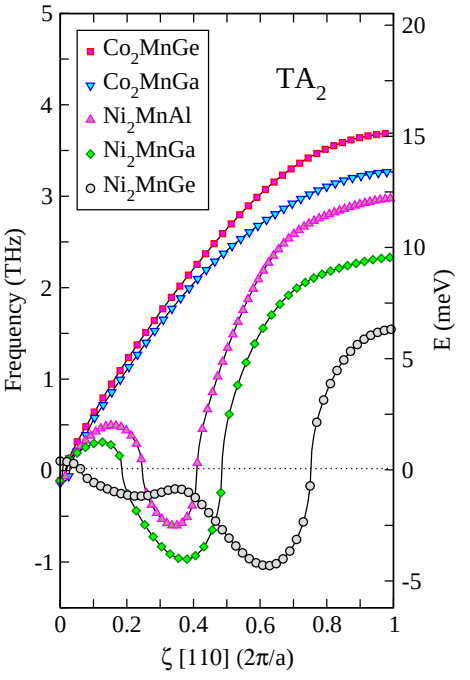

Fig. 3. Dispersion of the transverse acoustic phonon modes calculated for different alloys: Ni_2MnGa, Ni_2MnGe, Ni_2MnAl, Co_2MnGa and Co_2MnGe. Positions of the softening for Ni_2MnGa and Ni_2MnAl coinside which we relate to the same valence electron concentration of these alloys ($e/a = 7.5$). Increasing of e/a shifts the softening to larger ζ, while decreasing e/a shifts the softening towards the center of the Brillouin zone where Co_2MnGa and Co_2MnGe can be considered as limiting cases.

complete microscopic explanation of the martensitic modulated structures is not available which, however, is the key to understand the different properties of apparently similar Heusler alloys like Ni_2MnGa and Co_2MnGa. So far, one has tentatively related the modulated shuffling of the atoms and the phonon softening to the specific shape of the Fermi surface of Ni_2MnGa [12,13]. In this way the Kohn anomaly driven by the Fermi–surface nesting can lead to the structural instabilities of the crystal. Unfortunately this nesting picture does not give a comprehensive understanding of the micro-mechanics involved in the shuffling of the atoms on the atomic scale. It also does not allow a complete characterization of the expected strong coupling of the electrons and phonons. Finally atomic disorder, important for the stabilization of the modulated structures, might diminish the impact of nesting features.

With the aim to connect the electron and phonon properties of the Heusler alloys we have carried out a series of *ab-initio* investigations. Phonon dispersions of several Heusler alloys have been calculated in order to discuss differences between stable and unstable structures.

2. Computational details

In order to calculate the phonon dispersions we have used the direct force–constant method [5,6]. This method uses the forces calculated via the Hellmann-Feynman theorem in the total energy calculations for a supercell with periodic boundary conditions, which define to the corresponding dynamical matrix. The method works within the harmonic approximation and the accuracy of it strongly depends on the size of the considered supercell [5].

The Vienna *Ab-initio* Simulation Package (VASP) [7] has been used to perform the electronic structure calculations. The projector-augmented wave formalism (PAW), implemented in this package [8], leads to very accurate results compared to all-electron methods. The electronic exchange and correlation are treated by using the generalized gradient approximation.

All alloys considered in this work exist in the cubic $L2_1$ structure shown in Fig. 1(a) (in case of Ni_2MnGe the $L2_1$ structure has not been reported so far). All directions are refered to the cubic structure. We take five tetragonal cells shown in Fig. 1(b) and merge them together along the [110] direction giving a $1 \times 5 \times 1$ orthorhombic supercell. The five tetragonal unit cells allow for five k-points in the Brillouin zone along the [110] directions for which the calculated phonon fre-

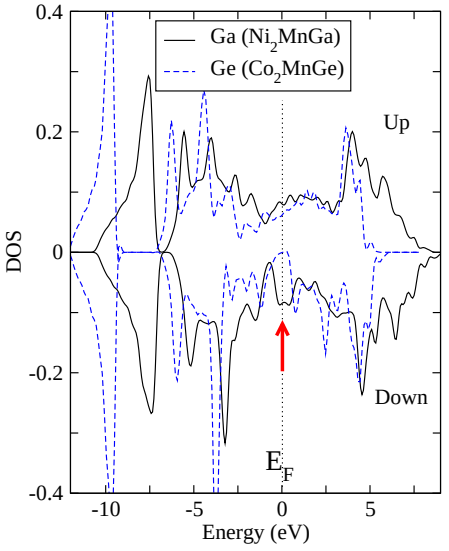

Fig. 4. Site projected electronic density of states of Ni_2MnGa and Co_2MnGe showing the difference in the spin-down electronic states close to the Fermi level of stable and unstable Heusler alloys. In Ni_2MnX alloys (X = Ga, Ge, Al, In) the peak marked by the arrow arises from p-states of the X atom, whereby the double peak structure is hybridization splitting. The X-projected $p\downarrow$-orbitals are coupled to the Ni-projected $d\downarrow$ states. We tentatively argue that this hybridization will be influence by the electron-phonon interaction.

quencies will be exact [5].

3. Discussion

The calculated phonon dispersions for cubic Co_2MnGe are shown in Fig. 2. Further dispersions not shown here have been obtained for Ni_2MnGa, Ni_2MnAl, Ni_2MnGe and Co_2MnGa [10,11]. In case of Ni_2MnGa and Ni_2MnAl the acoustic phonon modes soften in the range of ζ between $\approx$ 0.2-0.5 and 0.25-04, respectively. This incommensurate softening is observed in experimental studies and assigned to be at the origin of the modulations [9,13]. In case of Ni_2MnGe the softening is also present but the $L2_1$ structure of this crystal is not stable which leads to additional instability at small values of ζ. In contrast to that, Co_2MnGe (Fig. 2) and Co_2MnGa do not show an incommensurate phonon instability.

In order to compare how the softening appears in different Heusler alloys we show in Fig. 3 the calculated dispersions of the TA_2 phonon modes of all five crystals. We emphazise here the fact that the position of the softening can be related to the e/a ratio of the corresponding Heusler alloy.

Figure 4 shows Ga and Ge site projected DOS of Ni_2MnGa and Co_2MnGe, respectively. We note here that the main origin for the phonon instability can be related to nesting of the minority-spin states close to the Fermi level [12]. The stable systems do not show corresponding nesting. However, our calculations show additional features primarily related to the origin of the Fermi–surface nesting. Namely, in all unstable Heusler alloys we find hybridization of unomalously low-lying optical and acoustic phonons. We expect that this feature leads to an additional strengthening of the electron-phonon coupling because of localized mode–electron coupling. In particular, this coupling might enhance the interaction of the Ni-d and Ga-p minority-spin states. The electron-phonon interaction will flatten corresponding d bands of Ni right at the Fermi level leading to a nesting shape of the Fermi surface allowing for structural instrabilities and the formation of martensitic modulated structures. In conclusion we can therefore say that the main driving force for martensitic transformations in MSM alloys is still at debate and not a completely solved question.

4. Acknowledgements

Financial support by the German Science Council (GRK 277 and SFB 491) is very much acknowledged.

References

[1] K. Ullakko, J. Huang, C. Kantner, R. O'Handley, V. Kokorin, Appl. Phys. Lett. **69** (1996) 1966.
[2] A. Sozinov, A. A. Likhachev, N. Lanska, K. Ullakko, V. K. Lindroos, J. Phys. IV France **112** (2003) 955.
[3] Z. Wei, G.Engdahl, in: Proc. 7th Int. Conf. New Actuators, ACTUATOR 2000, Bremen, Germany, 2000, p. 42.
[4] I. Takeuchi, O. O. Famodu, J. C. Read, M. A. Aronova, K.-S. Chang, C. Craciunescu, S. E. Lofland, M. Wuttig, F. C. Wellstood, L. Knauss, A. Orozco, Nature Materials **2** (2003) 180.
[5] K. Parlinski, Z. Q. Li, Y. Kawazoe, Phys. Rev. Lett. **78** (1997) 4063.
[6] K. Parlinski, PHONON, Cracow, Poland (2002).
[7] G. Kresse, J. Furthmueller, Phys. Rev. B **54** (1996) 11169.
[8] P. E. Blöchl, Phys. Rev. B **50** (1994) 17953.
[9] L. Mañosa, A. Planes, J. Zarestky, T. Lograsso, D. L. Schlagel, C. Stassis, Phys. Rev. B **64** (2001) 024305.
[10] A. T. Zayak, P. Entel, J. Enkovaara, A. Ayuela, R. M. Nieminen, Phys. Rev. B **68** (2003) 132402.
[11] T. Büsgen, J. Feydt, R. Haßdorf, S. Thienhaus, M. Moske, M. Boese, A. Zayak and P. Entel, Phys. Rev. B, accepted.
[12] Yongbin Lee, Joo Yull Rhee, and B. N. Harmon, Phys. Rev. B **66** (2002) 054424.
[13] C. Bungaro, K. M. Rabe, A. D. Corso, Phys. Rev. B **68** (2003) 134104.